

# PATENT SPECIFICATION

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(54) A PROCESS FOR IMPREGNATING MICROPOROUS FILMS, AND THE PRODUCT PRODUCED THEREBY

(71) We, BIAX-FIBERFILM CORPORATION, a Corporation organized and existing under the laws of the State of Wisconsin, United States of America, of 5 1066 American Drive, Neenah, Wisconsin, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to 10 be particularly described in and by the following statement:

This invention relates to a process for impregnating microporous films, and the product produced thereby, preferably by stretching an impregnated film of a synthetic thermoplastics polymer or blend thereof, and more particularly to a process for producing impregnating microporous films of a synthetic thermoplastics polymer 20 or blend thereof by cold drawing such an impregnated film.

A microporous sheet or film is useful as a printing substrate, such as synthetic paper, as a substitute for leather, as a highly 25 fibrillated sheet which can easily be shredded into fine fibrils to be used as substitutes for paper-making pulps, or as a filter material, such as a battery separator.

Porous paper having sufficient wet-strength and impregnated with nicotinic acid, such as disclosed in U.S. Patent No. 30 2,491,646, is used as a meat-interleaf paper. In industry, meat-interleaf paper is stacked between freshly cut steaks to prevent 35 formation of dark brown colour, and preserve the fresh red meat colour during storage. The function of the porosity of the paper is to make small amounts of oxygen available to the meat pigment myoglobin; 40 oxygen is needed to retain the myoglobin in the red state. A chemical additive, nicotinic acid, prolongs the time for which the red colour is retained by a catalytic mechanism not entirely understood. Other chemicals 45 are known from the patent literature to produce similar effects (U.S. Patent No. 3,867,558: gamma-pyrone; U.S. Patent No.

3,615,691: tetrazole; U.S. Patent No. 3,266,909: glutamic acid salt; U.S. Patent No. 2,863,777: pyridine/ascorbic acid).

Many polymeric materials or especially blends thereof are known to undergo fibrillation and/or pore formation upon stretching or drawing. A number of such blends are described in U.S. Patent Nos. 3,697,367 and 3,511,742. Such pore formation may result from different causes, such as separation of phases of incompatible polymer blends, or separation or inorganic polymer fillers such as clay or titanium dioxide from the polymer matrix due to stress concentration. It is most common in such systems that the maximum pore formation effect occurs at a draw temperature which is relatively low for the particular polymer system. When the same polymer or blend thereof is stretched at higher temperatures the pore formation diminishes and a denser film results.

At temperatures where pore formation occurs accompanied by a decrease in density, the draw tension also increases. Draw tension or yield strain also increases with increasing draw rate or operating speed, and reaches the breaking strength of the base film at speeds which are slow and uneconomical for conventional systems used for stretching or drawing of films. Operating a conventional stretching system, such as longitudinal stretching by Goudet rolls and lateral stretching by tenter frames, under tensions which approach the breaking strength of the base film often causes breaks and frequent interruptions of the process. Extrusion speeds are uneconomically slow; for instance, an acceptable draw rate of 200 cm/min in a single longitudinal draw step over Goudet rolls for a 90 wt.% isotactic polypropylene — 10 wt.% polystyrene (see Example 1), would limit the extrusion rate (for a 3' linear die at a draw ratio of 2.0 and a film thickness of 100 micron) to 23.2 lb/hr.

In British Patent No. 1,521,579, there is

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- disclosed a method for fibrillating polymer blends of incompatible polymers or filled polymers to form fibrillated or microporous structures by cold drawing at high tension such blends or polymers. Such microporous structures are very difficult to impregnate with solvents or solutions of chemicals because of the small size of the pores. Surface tension and capillary action prevent the entry of solutions. Thus, a microporous film made by the method described in British Patent No. 1,521,579, while usually permeable to vapours, is not permeable to liquids. Permeability indicates complete open-cell pore structure of the fibrillated films.
- The present invention in one aspect provides a process for longitudinally stretching incremental portions of a film comprising a blend of a thermoplastics orientable polymer with an incompatible second phase selected from an incompatible polymer or inorganic material, or a polymer matrix having an inorganic filler, which comprises:
- (a) passing the said film through a solution of an impregnating chemical;
  - (b) introducing the said film of step (a) into a nip of interdigitating rollers having grooves substantially parallel to the axis of the said rollers;
  - (c) controlling the velocity of introduction of the said film into the said nip to assume and maintain a velocity substantially identical to the surface velocity of the said rollers thereby to longitudinally stretch incremental portions of the said film; and
  - (d) collecting the thus formed film.
- The invention in another aspect provides a process for bi-axially stretching incremental portions of a film comprising a blend of a thermoplastics orientable polymer with an incompatible second phase selected from an incompatible polymer or inorganic material, or a polymer matrix having an inorganic filler, which comprises:
- (a) passing the said film through a solution of an impregnating chemical;
  - (b) introducing the said film into a nip of interdigitating rollers having grooves parallel to the axis of the said rollers;
  - (c) controlling the velocity of introduction of the said film into the said nip to assume and maintain a velocity substantially identical to the surface velocity of the said rollers thereby to longitudinally stretch incremental portions of the said film;
  - (d) withdrawing the said film from the said rollers at a velocity greater than the rotational velocity of the rollers;
  - (e) introducing the said film into a nip of interdigitating rollers having grooves substantially perpendicular to the axis of the said rollers;
  - (f) controlling the velocity of introduction of the said web into the said nip to assume and maintain a velocity substantially identical to the surface velocity of the said rollers thereby to laterally stretch incremental portions of the said web;
  - (g) withdrawing the said web from the said rollers at a velocity substantially corresponding to the velocity of introduction; and
  - (h) collecting the thus stretched film.
- The invention in a further aspect provides a process for laterally stretching incremental portions of a film comprising a blend of a thermoplastics orientable polymer with an incompatible second phase selected from an incompatible polymer or inorganic material, or a polymer matrix having an inorganic filler, to produce a microporous film, which comprises:
- (a) passing the said film through a solution of an impregnating chemical;
  - (b) introducing the said film of step (a) into a nip of interdigitating rollers having grooves substantially perpendicular to the axis of the said rollers;
  - (c) controlling the velocity of introduction of the said film into the said nip to assume and maintain a velocity substantially identical to the surface velocity of the said rollers to prevent narrowing of the film prior to introduction into the said nip thereby to laterally stretch incremental portions of the film by deflection of the film into the shape of the said grooves; and
  - (d) collecting the thus laterally stretched film.
- In the last mentioned aspect of the invention, the stretched film is preferably laterally extended prior to the step (d).
- Thus there is provided a process for impregnating a film of a blend of a thermoplastics orientable polymer with an incompatible second phase selected from an incompatible polymer or inorganic material followed by the selective stretching in a station provided with a set of groove rollers to form an opaque, low density, porous film. The groove pattern of the rollers is generally of a sinusoidal wave wherein the impregnated film is stretched in a manner to affect uniform stretching between contact points of the material to produce a material of larger dimension in the direction of stretch.
- In accordance with a preferred embodiment of the present invention, there is provided a process for impregnating a blend of a thermoplastics orientable polymer with an incompatible second phase selected from an incompatible polymer or

inorganic material followed by the stretching of such an impregnated film in a first and a second station wherein the first and second stations are provided with sets 5 of rolls having grooves parallel and perpendicular, respectively, to the axis of each set of rolls. The film of synthetic material is stretched in a manner to fibrillate such film to produce an opaque 10 low density porous sheet, an impregnated microporous sheet or film of thermoplastics material.

In a particularly preferred embodiment, 15 a plurality of stations are arranged in a preselected manner, as determined by product requirements, e.g. a multiplicity of sets of rollers having parallel grooves, perpendicular grooves, alternating parallel and perpendicular grooves, etc.

20 The impregnated microporous films produced by the process exhibit useful properties as speciality products depending on the impregnating chemicals.

The invention will be further described, 25 by way of example only, with reference to the accompanying drawings, wherein:

Figure 1 is a schematic side elevational view of a portion of an apparatus for carrying out the process of the present 30 invention;

Figure 2 is a schematic side elevational view of the remaining portion of the apparatus for carrying out the process of the present invention;

35 Figure 3 is an enlarged view of the film entering the rolls;

Figure 4 graphically illustrates a 40 sinusoidal curve; and

Figure 5 is a top view of the second station followed by another first station of the apparatus.

Drive and support assemblies and timing and safety circuits known and used by those skilled in the art have been omitted from 45 the drawings in the interest of clarity.

Referring to Figure 1, illustrating the front end of the apparatus for carrying out the process of the present invention, there is provided a supply roll 10 on which is 50 mounted a film 24 of a blend of thermoplastics orientable polymers with an incompatible second phase selected from an incompatible polymer or an inorganic material. The film is coursed about rollers 55 through a coating or impregnating liquid or solution, generally indicated as "S", contained in a vessel 15. The coated or impregnated film is then coursed between a nip 14 of a pair of rolls 16 having a plurality 60 of tips 18 forming grooves 20 parallel to the axis of the rolls 16, as seen in Figure 3. The film is maintained against the lower grooved roll 16 by a pair of press rolls 22 to ensure that the velocity  $V_1$  of the film is 65 substantially identical to the surface

velocity  $V_1$  of the grooved rolls 16. The grooves 20 of the rolls 16 are intermeshed like gears, as known to those skilled in the art. As the film enters the nip 14, the film assumes the shape of the grooves 20 and is stretched (see Figure 3) by a factor determined by the length of the sinus wave "l" (see Figure 4) of the groove divided by the distance "w" between contact points of each respective groove tip, since the film is prevented from slipping by the press rolls 22 to prevent the introduction of more material, as is more commonly practiced in the corrugating art.

70 The draw ratio ( $l/w$ ) is calculated by the following equation:

$$l/w = l/\pi \sqrt{1+a^2 \cos^2 x} dx$$

where,  $a=\pi d/w$ , and  $d$ =groove depth. Thus, for  $d/w$  ratios of 1.0, 0.75 and 0.5 the draw ratios are 2.35, 2.0 and 1.6, respectively. The longitudinal draw rate is defined by the 75 following equation:

$$\text{draw rate} = V_2 - V_1$$

where

$V_1$ =film velocity entering rolls; and

$V_2$ =film velocity leaving rolls.

80 The Actual Draw Rate (ADR) for longitudinal or lateral stretching is calculated by the following equation:

$$ADR = \frac{(draw ratio - 1)V}{4 d/w \sqrt{R/d - l/4}} \quad 95$$

where,

$d$ =groove depth;

$w$ =distance between tips;

$l$ =length of sinusoidal wave;

the draw ratio= $l/w$ ;

90  $V$  is the velocity of the film entering the nip of the rollers; and

$R$  is the radius of the rollers.

100 The roller speed can be calculated as follows:

$$ADR \cdot 4 d/a \sqrt{R/d - l/4} \quad 105$$

$$V = \frac{\text{draw ratio} - 1}{\text{draw ratio} - 1}$$

Thus, if the critical ADR for a composition operating at about 80% of breaking tension is 100 cm/min., and  $d/w=1$ , draw ratio is 2.25,  $R$  is 10 cm. and  $d=0.3$  cm., then  $V_1=ADR \cdot 18.41=1841$  cm/min., which is 18.41 times faster than permissible with Goudet rolls. For a 6 inch wide film die making 4 mil. film, an extrusion rate of 565 lbs/hr. can be obtained vice 30.4 lbs/hr.

110 The film 24 after passage through the nip 14 of the rolls 16 is pulled away by a pair of tension rollers 26 having a surface velocity 115

5  $V_2$  greater than the surface velocity of the rollers 16, but not greater than a factor of the draw ratio affected in the nip 14 of the rollers 16. The length of the film is therefore increased by this factor.

10 It is noted that the film does not undergo narrowing while being longitudinally stretched or extended, as is the case with conventional roller systems. It is apparent to one skilled in the art that the film may sequentially pass through a plurality of pairs of grooved rollers 16 to further stretch lengthwise the film 24 prior to lateral stretching as more fully described 15 hereinafter.

15 Referring now to Figure 2, the longitudinally stretched film 24 from the first station is introduced into a nip 28 formed by a pair of rolls 30 having a plurality of tips 32 forming grooves 34 parallel to the circumference of the rolls 30 in a second station of the apparatus. The film 24 is caused to be coursed into the nip 28 by a pair of press rolls 36 which holds the film 24 against the lower roll 30 to thereby prevent the film 24 from narrowing prior to introduction. Once in the nip 28, the film 24 assumes the shape of the groove pattern and becomes laterally stretched by a factor 20 of the draw ratio determined in a manner similar to the draw ratio discussed with reference to Figure 1.

25 The crimp pattern is flattened out by stretching the sheet 37 laterally by means of tenter clamps or curved Mount Hope rolls, generally indicated as 39 such as known and used in the art. After passage through the nip 28, the film is pulled away by a pair of 30 tension rollers 38.

35 In the second station, i.e. lateral stretching, the sheet is wound up at about the same velocity as the feed velocity with the product being collected on a roll 40. For best results, the longitudinal and lateral stretching steps are repeated alternately through multiple passes each having a relatively low draw ratio, until the total permissible draw ratio is reached. The 40 number of longitudinal and lateral passes, as well as the extent of the stepwise draw ratios, can be chosen so that a final film is obtained with the desired properties. Figure 5 illustrates the film 37 being further coursed into another set of rolls 42 having grooves 44 parallel to the axis for further longitudinal stretching, which could be subsequently followed by another lateral stretching.

45 As hereinabove indicated, microporous filters have many industrial uses, for example as bacteria or enzyme filters, or battery separators. Besides wetting agents, other chemicals such as insecticides, fungicides, deodorants, disinfectants, drugs 50 and flame retardants, can be impregnated

5 into such a microporous film for later release during use.

10 The invention will be further described with reference to the following illustrating Examples.

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#### Example I

15 A 0.004" thick film (4" x 4") comprised of 85 wt.% polypropylene and 15 wt.% clay coated with a solution of a wetting agent (10 wt.% polyethylene oxide in methanol) was introduced at room temperature through a pair of grooved rolls (as shown in Figure 1). The grooves had an approximate sinusoidal shape and were 3 mm. deep and 3 mm. apart and produced a draw ratio of about 2. When the film was stretched to conform 20 with the shape of the grooves, 8 groove tips simultaneously engaged the film. The film was introduced into the nip of the intermeshing grooved rolls rotating at 60 RPM to produce a feed velocity  $V_1$  of 1914 cm./min. and was wound at 3828 cm./min. The actual film draw rate was 120 cm./min. The film was passed through twice in each direction and stretched to a dimension of 6.5" x 6.5" and having a thickness of 0.0025". The solvent was evaporated and the resulting film sample tested for water permeability. The film sample was cut to a circle to fit a 3" Buchner funnel. A suction of 20 mm. vacuum was applied to the funnel with 10 ml. of water added to the funnel. Water was filtered in 12 min. through the porous film.

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#### Example II

100 The procedure of Example I was repeated without the impregnation step and produced a sample stretched to a dimension of 6.5" x 6.5" and having a thickness of 0.004 inch—calculated porosity of 39%. The film was similarly tested for water permeability in a manner substantially similar to that of Example I; however, water did not penetrate through the film in a period of 24 hours although exhibiting air permeable properties.

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#### Example III

115 A sample prepared in accordance with Example II was boiled in a wetting agent solution for one hour to effect coating of the pores by the wetting agent and to cause water to penetrate through the porous film. The solvent was dried off and the film tested for filtration of water as described above. Water would not pass through the film indicating that the wetting agent solution merely coated the pores near the surface of the film, but did not penetrate deeply into the film, when applied after the stretching process.

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**Example IV**

Three sheets of the porous film of Example I were stretched to test the effect of retaining the red colour of freshly cut meat. One sheet (A) was not coated. A second sheet (B) was coated with a 2% solution of nicotinic acid in water, with excess solution being wiped off the surface to avoid the presence of unabsorbed chemical. A third sheet (C) was coated at room temperature with a nicotinic acid solution prior to stretching. Steaks of freshly cut beef was stacked on top of each other, with the film sheets interleaved between the meat surfaces. The meat surfaces in contact with films A and B turn dark within 2 hours of storage in a refrigerator at 30°F. The meat surface in contact with film C retained its fresh red colour for 24 hours and was only slightly brown after 48 hours.

**Example V**

Films B and C of Example IV were extracted with 50% water/50% acetone to determine the amount of nicotinic acid extracted (infrared spectroscopy of the extract and related to the film weight). The results were:

Sample B — 0.05% nicotinic acid.  
Sample C — 1.02% nicotinic acid.

While the present invention has been described with reference to the passage of a film through a first longitudinal stretching station and thence a lateral stretching station, it is apparent that such stations may be altered with the film being first introduced into a lateral stretching station. Further, the film may be subjected to a plurality of longitudinally orientated stretching rolls. It will also be appreciated that the grooves need not be exactly parallel or perpendicular as long as the grooves intermesh.

It will be appreciated that the grooved roll drawing permits multiple simultaneous draw necks which allow for further actual speed where draw tension is high. At high draw tension (low temperature), the fibrillation phenomenon occurs which is highly desirable for porous films. Additionally, the grooved roll drawing permits a partial draw (draw below the natural draw ratio) in multiple stages thereby further reducing the actual draw rate and increasing the production rate. Still further defects in the base film, i.e. gels or holes, are carried through the grooved roll drawing with no interruption in the process as distinguished from drawing in conventional Goudet and tenter frame drawing wherein such defects usually result in breaks and the necessity for subsequent shutdown.

**WHAT WE CLAIM IS:—**

1. A process for longitudinally stretching incremental portions of a film comprising a blend of a thermoplastics orientable polymer with an incompatible second phase selected from an incompatible polymer or inorganic material, or a polymer matrix having an inorganic filler, which comprises:
  - a) passing the said film through a solution of an impregnating chemical;
  - b) introducing the said film of step (a) into a nip of interdigitating rollers having grooves substantially parallel to the axis of the said rollers;
  - c) controlling the velocity of introduction of the said film into the said nip to assume and maintain a velocity substantially identical to the surface velocity of the said rollers thereby to longitudinally stretch incremental portions of the said film; and
  - d) collecting the thus formed film.
2. A process as claimed in Claim 1, wherein the withdrawal velocity of step (c) is not greater than a factor of the draw ratio of the said nip.
3. A process for bi-axially stretching incremental portions of a film comprising a blend of a thermoplastics orientable polymer with an incompatible second phase selected from an incompatible polymer or inorganic material, or a polymer matrix having an inorganic filler, which comprises:
  - a) passing the said film through a solution of an impregnating chemical;
  - b) introducing the said film into a nip of interdigitating rollers having grooves parallel to the axis of the said rollers;
  - c) controlling the velocity of introduction of the said film into the said nip to assume and maintain a velocity substantially identical to the surface velocity of the said rollers thereby to longitudinally stretch incremental portions of the said film;
  - d) withdrawing the said film from the said rollers at a velocity greater than the rotational velocity of the rollers;
  - e) introducing the said film into a nip of interdigitating rollers having grooves substantially perpendicular to the axis of the said rollers;
  - f) controlling the velocity of introduction of the said web into the said nip to assume and maintain a velocity substantially identical to the surface velocity of the said rollers thereby to laterally stretch incremental portions of the said web;
  - g) withdrawing the said web from the said rollers at a velocity substantially corresponding to the velocity of introduction; and
  - h) collecting the thus stretched film.
4. A process as claimed in Claim 3, wherein the steps (b) to (g) are repeated prior to the step (h).
5. A process as claimed in Claim 4,

- wherein the steps (e) to (g) are effected prior to the steps (b) to (d).
6. A process for laterally stretching incremental portions of a film comprising a blend of a thermoplastics orientable polymer with an incompatible second phase selected from an incompatible polymer or inorganic material, or a polymer matrix having an inorganic filler, to produce a microporous film, which comprises:
- (a) passing the said film through a solution of an impregnating chemical;
  - (b) introducing the said film of step (a) into a nip of interdigitating rollers having grooves substantially perpendicular to the axis of the said rollers;
  - (c) controlling the velocity of introduction of the said film into the said nip to assume and maintain a velocity substantially identical to the surface velocity of the said rollers to prevent narrowing of the film prior to introduction into the said nip thereby to laterally stretch incremental portions of the film by deflection of the film into the shape of the said grooves; and
  - (d) collecting the thus laterally stretched film.
7. A process as claimed in Claim 6, wherein the said stretched film is laterally extended prior to the step (d).
8. A process as claimed in any of Claims 1 to 7, wherein the said resulting film is cut into sheets.
9. A process as claimed in any of Claims 1 to 8, wherein the said impregnating chemical is a solution of nicotinic acid.
10. A process according to Claim 1 for longitudinally stretching incremental portions of a film, substantially as herein described with reference to Figures 1 and 3 of the accompanying drawings.
11. A process according to Claim 3 for bi-axially stretching incremental portions of a film, substantially as herein described with reference to Figures 1, 2, 3 and 5 of the accompanying drawings.
12. A process according to Claim 6 for laterally stretching incremental portions of a film, substantially as herein described with reference to Figures 2 and 5 of the accompanying drawings.
13. A process according to Claim 1 for longitudinally stretching incremental portions of a film substantially as herein described in the foregoing Example 1.
14. The product of the process as claimed in any of Claims 1 to 13.
15. An interleaf for meat which comprises a stretched blend of a thermoplastics orientable polymer with an incompatible second phase selected from an incompatible polymer or inorganic material, or a polymer matrix having an inorganic filler, wherein the said material is impregnated with an antibrowning agent prior to stretching.
16. A product as claimed in Claim 15, wherein the said material is bi-axially stretched.
17. A product as claimed in Claim 15 or 16, wherein the said antibrowning agent is nicotinic acid.



Reference has been directed in pursuance of Section 9, Subsection (1) of the Patents Act 1949, to Patent Nos. 1,521,579 and 1,521,183.

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## COMPLETE SPECIFICATION

1 SHEET

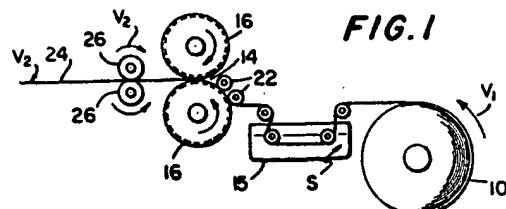
*This drawing is a reproduction of  
the Original on a reduced scale*

FIG. 1

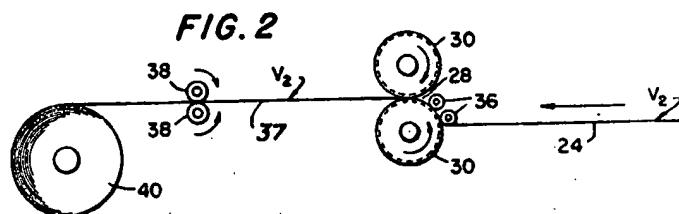


FIG. 2

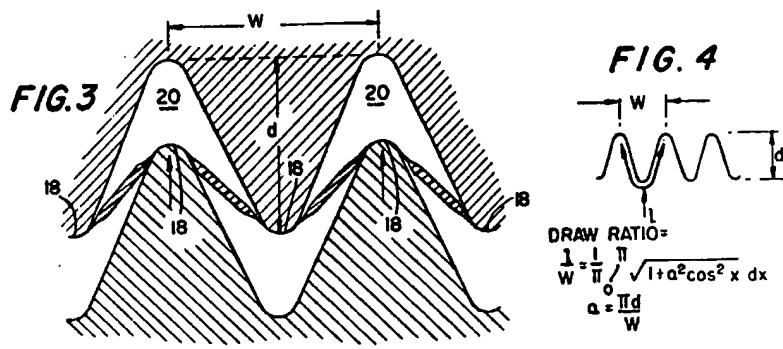


FIG. 4

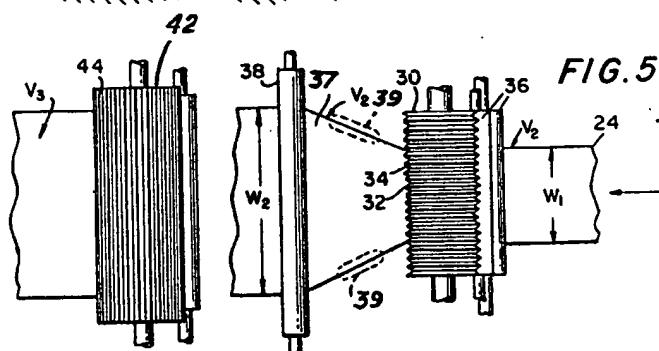
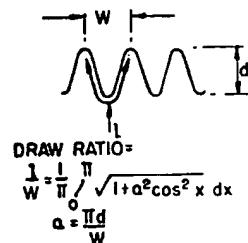


FIG. 5